Criticality and phase behavior in the restricted-primitive model electrolyte: description of ion association

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Ion association is incorporated into the restricted-primitive model (RPM) electrolyte to account for the strong attraction between unlike ions. Two methods are investigated within the McMillan-Mayer framework: first is the binding mean-spherical approximation (BIMSA) based on the Wertheim Ornstein-Zernike integral equation formalism; and the second is the combination of the BIMSA with a simple interpolation scheme (SIS) based on the Wertheim thermodynamic perturbation theory. The latter gives a better description. Four different association constants are used to calculate the degree of dissociation, the critical point and the vapor-liquid coexistence curve. An increase in the association constant leads to a lower critical temperature and a higher critical density, and better agreement with computer simulations. When unlike ions are fully paired, corresponding to a charged hard dumbbell (CHDB) system, we obtain the best agreement with the most recent computer simulations of the RPM electrolyte.

I. INTRODUCTION

It has been recognized for decades that ion association is an important effect in determining criticality and phase behavior of an electrolyte due to strong electrostatic attraction between ions of unlike charges. This effect is far from linear in terms of the strength of electrostatic interaction. The Debye-Hückel (DH)[1] theory and the mean-spherical approximation (MSA)[2,3] theory for electrolytes are essentially linearized Poisson-Boltzmann theories; they yield the correct Coulomb screening of long-length scales but cannot capture the nonlinear effect of ion association. Since the early days of the last century, various methods have been suggested to take ion association into account. In 1926, Bjerrum[4] added chemical association of ions into the DH theory. In the 1980s, Ebeling and Grigo (EG)[5] combined ion pairing with the MSA through the mass action law (MAL) and the second ionic virial coefficient. In this method, the ion pair is assumed to be an ideal component, i.e., its activity coefficient is unity. Later, in a similar manner, Gillan[6], Tani and Henderson[7], and Pitzer and Schreiber[8] evaluated the effect of ion association, including pairs and higher mers. For a detailed historic account, see recent reviews[9-13].

In recent years, several theoretical methods have been proposed in which the ion pairing is based on the addition of the *ad hoc* chemical-association model of Bjerrum and EG for the restricted-primitive model (RPM) of size-symmetric electrolytes. Fisher and Levin[14,15] extended DH theory by considering the solvation of dipolar ion pairs in an ionic fluid (dipole-ion interactions). When the hard core of the ions is neglected, the resulting Debye-Hückel-Bjerrum-Dipole-Ion (DHBjDI) theory gives a fairly good critical point and coexistence curve when compared with Monte Carlo (MC) simulation data[18]. DHBjDI model is probably quantitatively the most successful theory for the RPM electrolyte presently available. Careful studies[12],

however, found that the hard-core contribution is important in determining the phase coexistence of electrolytes. However, inclusion of the hard core into DHBjDI the Debye-Hückel-Bjerrum-Dipole-Ion-Hard-Core (DHBjDIHC) model is in poorer agreement with MC simulation results. Comparison with the latest high precision MC simulation data[19] shows that large deviations are found for both DHBjDI and DHBjDIHC.

Stell and coworkers[16,17] proposed the pairing MSA on the basis of a simple interpolation scheme (SIS)[20]. In the SIS the cavity correlation function for an associating fluid remains nearly the same as that of the dissociated fluid. This approximation is equivalent to the Wertheim first-order thermodynamic perturbation theory[21] that has been widely used to study thermodynamic properties of associating fluids and chain-like macromolecules. The ion pairing MSA was extended by adding the ion-dipole interactions to model the RPM electrolyte[16,17]. Because in the MSA the excluded-volume is treated correctly, we expect that this method will give better results than DHBjDI. Unfortunately, the calculated critical point and coexistence curve are less satisfactory. Stell and coworkers concluded that the agreement of DHBjDI with MC simulation was largely fortuitous.

Recently, Guillot and Guissani[12], and Schröer and coworkers[22,23], incorporated dipole-dipole interactions and dipolar screening to account for the dielectric effect. But worse results were obtained; the calculated critical temperature is too high, the critical density is too low and the coexistence curve is too narrow when compared with MC simulation results.

In this work, we present two methods to model criticality and phase behavior in the RPM electrolyte. First, the effect of ion association is included using the binding mean-spherical approximation (BIMSA) developed earlier[24,25]. The salient feature of the BIMSA is that it satisfies the exact fully associated zero density DH limit; that is, if two ions associate, the

limiting osmotic coefficient is given by the DH expression for an ion with a charge equal to the sum of the two associating ions. The associative mean-spherical approximation (AMSA), basically the BIMSA, was briefly described by Raineri *et al.*[26] for size-asymmetric primitive model electrolytes. We use first the analytical solution of the BIMSA expressed in terms of a screening parameter Γ^B that is a function of the degree of dissociation. When Γ^B is replaced by Γ without association, the BIMSA reduces to the SIS. Second, we use a combination of the BIMSA with the SIS, which gives a better critical point and a better coexistence curve. Section II presents the basic model and theoretical framework. Section III shows calculated results for four versions of the association constant, including full association corresponding to the charged hard dumbbell (CHDB) system[27]. A discussion and concluding remarks is given in Section IV.

II. MODEL AND THEORY

At the McMillan-Mayer level, the RPM electrolyte is represented by charged hard spheres with identical diameters σ in a continuous dielectric medium with permittivity ε. The number density of the hard spheres is $2\rho_0$; half of the species have a charge $+ze$ and the other half $-ze$ ($e=1.602\times10^{-19}\,\mathrm{C}$ is the elementary charge). The interaction between two particles consists of a hard-sphere repulsion and an electrostatic potential:

$$u_{ij}(R) = \begin{cases} \infty & R < \sigma \\ \dfrac{z_i\, z_j\, e^2}{4\pi\varepsilon R} & R \geq \sigma \end{cases}, \tag{1}$$

where R is the center-to-center distance. The ion association between unlike ions is modeled using Baxter's sticky-point potential inside the hard core σ^-. Only pairs are allowed (no trimers or higher mers).

Suppose a is the degree of dissociation, then the number density of free ions is $r_+ = r_- = r_0 a$ and that of neutral ion pairs is $r_p = r_0(1-a)$. The mass action law (MAL) is:

$$K = \frac{r_p}{r_+ r_-} = \frac{1-a}{r_0 a^2},$$ (2)

or

$$r_p = \frac{2K r_0^2}{1+2K r_0 + \sqrt{1+4K r_0}} = \frac{1+2K r_0 - \sqrt{1+4K r_0}}{2K},$$ (3)

where the stoichiometric association constant K depends on density at a given temperature. K can be separated into two parts: $K = K^0 K^g$ in which $K^g = g_+ g_- / g_p$ is the ratio of the activity coefficients of the free ions to that of the neutral pair. As we will see, correlation functions can be used to calculate K^g instead of the individual activity coefficients, of which the associating species is difficult to estimate. The thermodynamic association constant K^0, a constant at given temperature, is the infinite-dilute limit of K. We chose an approximation given by Ebeling[28] for K^0 such that the second ionic virial coefficient is recovered:

$$K_{Eb}^0 = 8 p s^3 \sum_{m=2}^{\infty} \frac{(T^*)^{-2m}}{(2m)!(2m-3)} = 4 p s^3 \int_0^1 dt \left[e^{t/T^*} + e^{-t/T^*} - (t/T^*)^2 - 2 \right]/t^4,$$ (4)

where $T^* = 4 p e s / b e^2 z^2$ is the reduced (dimensionless) temperature with $b = 1/k_B T$ and k_B (Boltzmann constant) $=1.38\times 10^{-23} \text{JK}^{-1}$. The degree of dissociation near the critical point calculated from K_{Eb}^0 is too large[5,16,17]. As suggested by Raineri *et al.*[26], two alternate thermodynamic association constants K_{OS}^0 [29] and K_{Fu}^0 [30] may be used to repair this deficiency. Following Raineri *et al.*[26], we chose:

$$K_{OS}^0 = 3 K_{Fu}^0 = 12 K_{Eb}^0.$$ (5)

Figure 1 shows the effect of reduced temperature T^* on these thermodynamic association constants; from bottom to top, they are K_{Eb}^0, K_{Fu}^0 and K_{OS}^0. All are large at low T^* and decrease with increasing T^*, indicating strong ion association at low T^*.

As found from MC simulation[19,31,32] the structure of the RPM electrolyte is largely that of the CHDB in both vapor and liquid phases. These two models have a similar critical point and similar phase behavior suggesting that we can assume full association between anion and cation ($a = 0$, $K_{fa}^0 = \infty$) and ignore free ions as a first approximation to model the RPM, as shown earlier[27].

The model above for electrolytes with Baxter's sticky potential, called the sticky-electrolyte model (SEM), was studied extensively using the Ornstein-Zernike (OZ) integral equation with a hybrid approximation PY/MSA or HNC/MSA.[33-35] Recently[24,25], we reported an analytical solution of the BIMSA by solving the Wertheim Ornstein-Zernike (WOZ) integral equation[21]. Unlike the usual OZ derived from Mayer density expansion, the WOZ is derived from an activity/fugacity expansion and can account properly for saturation effects in which only one bond is allowed between ions. This formalism includes the fraction of bonded sites obtained from the MAL.

From the BIMSA, the Helmholtz energy density f has four contributions from, respectively, the ideal gas, the hard-sphere repulsion, the MAL and the electrostatic interactions:

$$f = f^{id} + f^{hs} + f^{mal} + f^{ele}. \tag{6}$$

The ideal-gas contribution is:

$$\boldsymbol{b} f^{id} = 2\boldsymbol{r}_0 \ln \boldsymbol{r}_0 - 2\boldsymbol{r}_0, \tag{7}$$

The hard-sphere repulsion contribution is obtained from the well-known Carnahan-Starling[36] equation of state:

$$b f^{\text{hs}} = \frac{2r_0 h(4 - 3h)}{(1 - h)^2}, \tag{8}$$

where $h = r^* p / 6$ ($r^* = 2r_0 s^3$, the reduced density) is the packing fraction of ions before association. The MAL contribution is:

$$b f^{\text{mal}} = 2r_0 \ln a + r_0 (1 - a). \tag{9}$$

The electrostatic-interaction contribution is obtained from the BIMSA[24]. However, to obtain the correct limit for a very dilute solution, the BIMSA was closed with the exponential approximation (BIMSA-EXP)[25] that gives:

$$b f^{\text{ele}} = -2\ell_B r_0 z^2 \frac{\Gamma^B}{1 + \Gamma^B s} + \frac{(\Gamma^B)^3}{3p}, \tag{10}$$

where $\ell_B = b e^2 / 4 p e$ is the Bjerrum length characterizing the dielectric property of the continuous medium. Γ^B is the screening parameter calculated from:

$$4(\Gamma^B)^2 (1 + \Gamma^B s)^3 = k^2 (a + \Gamma^B s), \tag{11}$$

where k is the inverse Debye screening length defined by $k = \sqrt{4 p \ell_B \sum r_k z_k^2}$. Without association, $a = 1$, Γ^B reduces to $\Gamma = (\sqrt{1 + 2sk} - 1)/2s$, the screening parameter in the usual MSA[2,3]. In this case, eq. (10) reduces to:

$$b f^{\text{ele}} = -2\ell_B r_0 z^2 \frac{\Gamma}{1 + \Gamma s} + \frac{\Gamma^3}{3p}. \tag{12}$$

From the BIMSA[25,37] K^g is given by:

$$K^g = g_{+-}(s) / g_{+-}^0(s), \tag{13}$$

where $g_{+-}(s)$ is the anion-cation contact pair correlation function from the exponential approximation and $g_{+-}^0(s)$ is the corresponding infinite-dilute limit:

$$g_{+-}(s) = g^{\text{hs}}(s)\exp\left[-\frac{\ell_B}{s}\frac{z_+z_-}{(1+\Gamma^B s)^2}\right], \tag{14}$$

where $g^{\text{hs}}(s) = (1-h/2)/(1-h)^3$ is the contact pair correlation function for a hard-sphere fluid from the Carnahan-Starling equation of state[36]. With eq. (14), eq. (13) becomes:

$$K^g = g^{\text{hs}}(s)\exp\left[\frac{\ell_B z_+ z_- \Gamma^B(2+\Gamma^B s)}{(1+\Gamma^B s)^2}\right]. \tag{15}$$

Equations (6-15) complete the BIMSA model for ion pairing in the RPM electrolyte based on the Wertheim Ornstein-Zernike integral equation. However, we can also use the pair MSA as proposed from the SIS. In the SIS, the cavity correlation function of an associating fluid is almost the same as that for a dissociated fluid. This approximation is equivalent to the Wertheim first-order thermodynamic perturbation theory[21]. In the SIS, electrostatic interaction is calculated from eq. (12) and K^g is given by:

$$K^g = y_{+-}^{\text{ref}}(s), \tag{16}$$

where $y_{+-}^{\text{ref}}(s)$ is the contact anion-cation cavity correlation function evaluated at $a=1$, the reference ionic fluid without association.

As an improvement to the SIS, we propose a simple interpolation between the SIS and the BIMSA; we denote this interpolation SIS/BIMSA. Electrostatic interaction, similar to the SIS, is calculated from eq. (12); however K^g is from eq. (15). As we will see, this combination gives better results.

III. RESULTS

Table I lists critical temperature T_c^*, critical density r_c^* in the RPM electrolyte and the degree of dissociation a_c at the critical point estimated from the BIMSA and the SIS/BIMSA

with four versions of thermodynamic association constant K^0; included for comparison are those from DH[1], DHBjDI[14], DHBjDIHC[14], MSA[2,3] and MC simulation[19]. Figure 2 shows the relationship between T_c^* and r_c^* from the various models. For either BIMSA or SIS/BIMSA, with increasing K^0 ($K_{Eb}^0 < K_{Fu}^0 < K_{OS}^0 < K_{fa}^0$), a_c decreases as expected, leading to lower T_c^* and higher r_c^*. For a given value of K^0, SIS/BIMSA results in a lower T_c^*, higher r_c^* and larger a_c than the BIMSA. As linearized theories, no ion association (i.e., $a_c = 1$) is contained in DH and MSA, and as a consequence they give too high a T_c^* but too low a r_c^*; indeed values that are far from the exact critical point. The DHBjDI and DHBjDIHC models both give fairly good T_c^* but too low a r_c^*. When $K^0 = K_{fa}^0 = \infty$, that is, when anion and cation associate fully into neutral pairs, SIS/BIMSA-fa gives the best prediction (0.0525, 0.0640) for the critical point, very close to MC simulation results (0.0496, 0.0792)[19]. These favorable results support the assumption that the RPM electrolyte may be modeled as the CHDB without taking free ions into account, as shown in recent MC simulations[19,31,32].

Figure 3 shows the vapor-liquid coexistence curve in the RPM electrolyte calculated from MSA, BIMSA (a), SIS/BIMSA (b) and MC simulations (open squares)[19]. From top to bottom, the corresponding thermodynamic association constant K^0 increases. For either BIMSA or SIS/BIMSA, with increasing K^0, the slopes of T^* with respect to r^* in both vapor and liquid phases decrease. At low temperature T^*, for BIMSA, the vapor and liquid phases change little with K^0; in contrast, for SIS/BIMSA, the liquid phase decreases with rising K^0. Given K^0, both the vapor and liquid phases from SIS/BIMSA are flatter than those from BIMSA, i.e., with lower slopes, because SIS/BIMSA gives lower T_c^*.

Figure 4 shows the vapor‑liquid coexistence curve in the RPM electrolyte calculated from MSA, BIMSA‑fa, SIS/BIMSA‑fa, DHBjDI[14], DHBjDIHC[14] and MC simulation (open squares)[19]. The slopes of the vapor phase from the MSA, BIMSA‑fa, DHBjDI and DHBjDIHC are too steep compared with MC simulation results; nevertheless, SIS/BIMSA‑fa gives much better results. In the liquid phase, DHBjDI gives a density that is too high while DHBjDIHC gives a density that is too low. Similar to the prediction for critical point, SIS/BIMSA‑fa gives the most successful prediction for the coexistence curve when the RPM electrolyte is modeled as the CHDB.

IV. DISCUSSION AND CONCLUSIONS

In this work two approximations, the BIMSA and the SIS/BIMSA, are presented for the study of the RPM electrolyte. Ion pairing between unlike ions is important in determining the critical conditions and the vapor‑liquid phase equilibrium. With increasing association constant, the critical temperature T_c^* decreases and the critical density r_c^* increases. Compared with the BIMSA, in general, the SIS/BIMSA gives a better critical point and coexistence curve. When unlike ions are fully paired, i.e., when the RPM electrolyte becomes to the CHDB, SIS/BIMSA‑fa gives the most successful quantitative prediction for the critical point and of the coexistence curve, consistent with the observation from computer simulation that the critical point and phase equilibrium of the RPM electrolyte are very similar to those of the CHDB.

The nature of the criticality in the RPM electrolyte — whether of the classical (mean field or van‑der‑Waals type, $a_{\text{classical}} = 0$), the Ising type ($a_{\text{Ising}} = 0.11$) or crossover between the two — remains controversial. Experimentally, both the classical[38,39] and the Ising type[40] critical behavior have been reported; another possible scenario concerns a crossover from the classical to

the Ising type[41]. However, by analyzing the heat capacity C_V near the critical point, one set of MC simulation results[42] suggested the classical criticality in the RPM electrolyte. Conversely, the Ising-type criticality was suggested from more recent MC simulation[43]. Indeed, in many studies by computer simulation, such as Ref. 19, *a priori* Ising-type criticality is assumed to estimate the critical point with a mixed-field finite-size scaling method. Ultimately, renormalization group theory may be required to describe this system properly.

At present, computer simulation studies are well ahead of the theories in this field. From cluster analysis, there appears to be an appreciable amount of neutral pairs and a linear (chain-like) alignment of alternatively charged ions. Theories based on the *ad hoc* chemical association model of Bjerrum and EG describe ion association only at the pairwise level; they cannot account for geometries and interactions in larger clusters.

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Table I. Critical temperature, critical density and the degree of dissociation from theories and MC simulation in the RPM electrolyte. [a] In Ref. 12, $T_c^* = 0.0521$ and $r_c^* = 0.0243$ if the hard core repulsion uses the Carnahan-Starling equation of state.

Theory	T_c^*	r_c^*	a_c	Date source
DH	1/16	$1/64\pi$	1	Ref. 1
DHBjDI	0.0574	0.0280	0.207	Ref. 14
DHBjDIHC	0.0554[a]	0.0260[a]	0.144	Ref. 14
MSA	0.0786	0.0144	1	Ref. 2,3
BIMSA-Eb	0.0723	0.0293	0.317	This work
BIMSA-Fu	0.0684	0.0375	0.149	This work
BIMSA-OS	0.0662	0.0415	0.082	This work
BIMSA-fa	0.0627	0.0471	0	This work
SIS/BIMSA-Eb	0.0707	0.0355	0.329	This work
SIS/BIMSA-Fu	0.0632	0.0511	0.155	This work
SIS/BIMSA-OS	0.0587	0.0590	0.084	This work
SIS/BIMSA-fa	0.0525	0.0640	0	This work
MC	0.0496	0.0792		Ref. 19

Figure Captions:

FIG.1. Effect of the reduced temperature on the thermodynamic association constant. From

bottom to top: K_{Eb}^0, K_{Fu}^0 and K_{OS}^0.

FIG.2. Critical temperature T_c^* and density r_c^* from theories and MC simulation for the RPM

electrolyte. Lines are drawn to guide the eye.

FIG.3. Vapor-liquid coexistence curve from theories and MC simulation for the RPM electrolyte.

(a) BIMSA; (b) SIS/BIMSA.

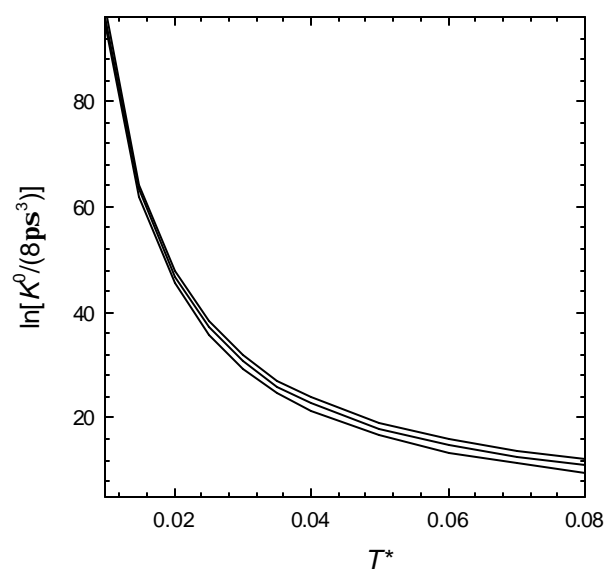FIG.4. Vapor-liquid coexistence curve from theories and MC simulation for the RPM electrolyte.
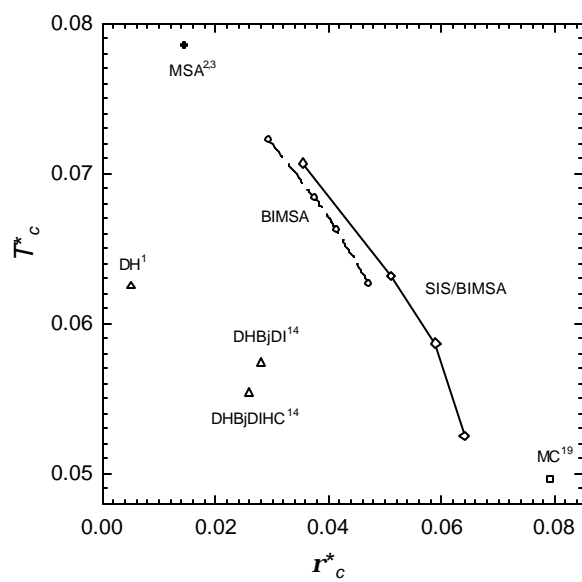
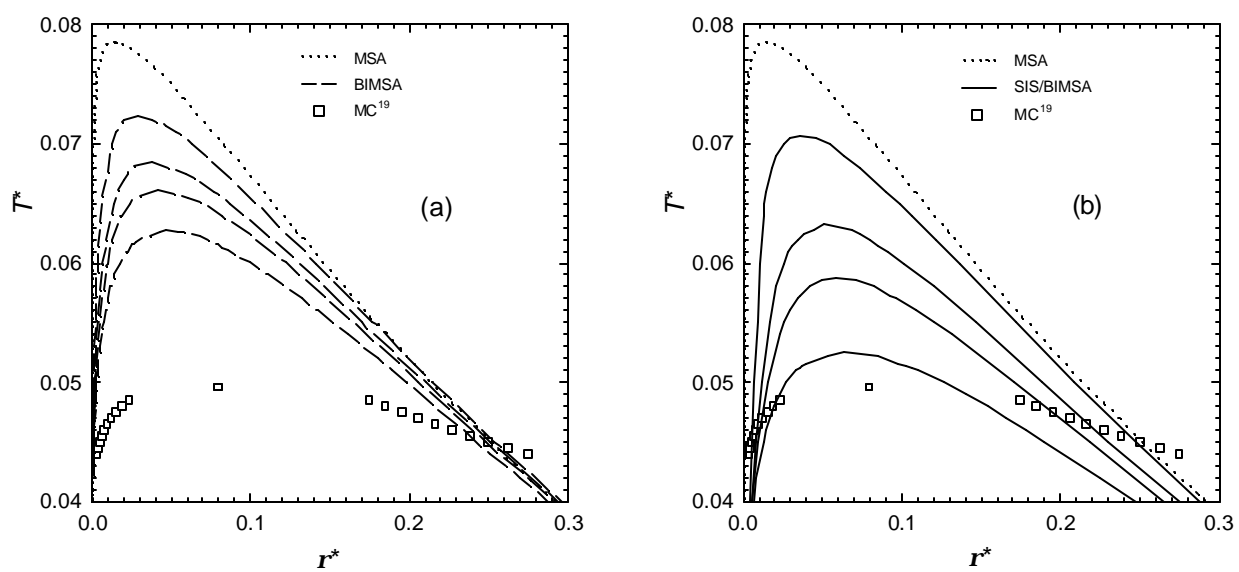FIG.1, by Jiang *et al.*

FIG.2, by Jiang *et al.*

FIG.3, by Jiang *et al*.

FIG.4,   by Jiang *et al*.